



Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2427028 A1 2002/05/02

(21) 2 427 028

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(36) Date de dépôt PCT/PCT Filing Date: 2001/10/04

(37) Date publication PCT/PCT Publication Date: 2002/05/02

(35) Entrée phase nationale/National Entry: 2003/04/25

(36) N° demande PCT/PCT Application No.: EP 2001/011482

(37) N° publication PCT/PCT Publication No.: 2002/034746

(30) Priorité/Priority: 2000/10/26 (MI2000A002321) IT

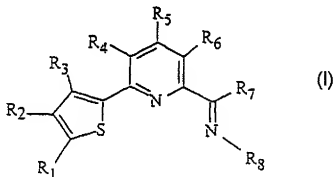
(51) Cl.Int.⁷/Int.Cl.⁷ C07D 409/04, C07F 15/06, C07F 15/02, C07F 19/00

(71) Demandeur/Applicant:
POLIMERI EUROPA S.P.A., IT

(72) Inventeurs/Inventors:
BIANCHINI, CLAUDIO, IT;
SOMMAZZI, ANNA, IT;
MANTOVANI, GIUSEPPE, IT;
SANTI, ROBERTO, IT;
MASI, FRANCESCO, IT

(74) Agent: ROBIC

(54) Titre : LIGANDS TRIDENTES ET COMPLEXES DE CES DERNIERS ET DE METAUX DE TRANSITION
(54) Title: TRIDENTATE LIGANDS AND RELATIVE COMPLEXES WITH TRANSITION METALS



(57) Abrégé/Abstract:

A description follows of ligands having general formula (I) wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 , the same or different, are selected from hydrogen, halogen, C_1 - C_{10} alkyl, C_6 - C_{15} aryl optionally halogenated, or adjacent pairs of R_i groups (with i ranging from 1 to 6) are bound to each other to give cyclic hydrocarbon structures condensed with the thiophene or pyridine ring; R_7 is selected from H, C_1 - C_{10} alkyl, C_6 - C_{15} aryl; R_8 is selected from C_1 - C_{10} alkyl and C_6 - C_{15} aryl. The complexes of the above ligands with transition metals are also described.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
2 May 2002 (02.05.2002)

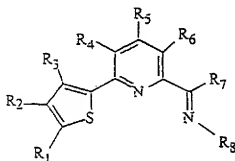
PCT

(10) International Publication Number
WO 02/34746 A3

- (51) International Patent Classification: C07D 409/04, C07F 19/00, 15/02, 15/06
- (74) Agents: DE GREGORI, Antonella et al.; Ing. Barzanó & Zanardo, Milano S.p.A., Via Borgonuovo, 10, I-20121 Milan (IT).
- (21) International Application Number: PCT/EP01/11482
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (22) International Filing Date: 4 October 2001 (04.10.2001)
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TO).
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: MI2000A002321 26 October 2000 (26.10.2000) IT
- (71) Applicant (for all designated States except US): POLIMERI EUROPA S.R.L. [IT/IT]; Via E. Fermi, 4, I-72100 Brindisi (IT).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): BIANCHINI, Claudio [IT/IT]; Via Fossombroni, 10, I-50136 Firenze (IT). SOMMAZZI, Anna [IT/IT]; Piazza Mazzini, 10, I-16030 Santa Margherita Ligure, Genova (IT). MANTOVANI, Giuseppe [IT/IT]; Via Guercino, 13, I-41034 Finale Emilia, Modena (IT). SANTI, Roberto [IT/IT]; Via Piazza d'Armi, 24/F, I-28100 Novara (IT). MASI, Francesco [IT/IT]; Via Galvani, 7, I-26866 Sant'Angelo Lodigiano, Lodi (IT).
- Published:
— with international search report
- (88) Date of publication of the international search report:
27 June 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: TRIDENTATE LIGANDS AND RELATIVE COMPLEXES WITH TRANSITION METALS



(I)

(57) Abstract: A description follows of ligands having general formula (I) wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 the same or different, are selected from hydrogen, halogen, C_1 - C_{10} alkyl, C_6 - C_{15} aryl optionally halogenated, or adjacent pairs of R_i groups (with i ranging from 1 to 6) are bound to each other to give cyclic hydrocarbon structures condensed with the thiophene or pyridine ring; R_7 is selected from H, C_1 - C_{10} alkyl, C_6 - C_{15} aryl; R_8 is selected from C_1 - C_{10} alkyl and C_6 - C_{15} aryl. The complexes of the above ligands with transition metals are also described.

5

TRIDENTATE LIGANDS AND RELATIVE COMPLEXES WITH TRANSITION
METALS

The present invention relates to new tridentate lig-
10 ands and the relative complexes with transition metals.

It is generally known in the art that ethylene, or
 α -olefins in general, can be oligomerized, polymerized or
copolymerized by means of low, medium or high pressure
processes, with heterogeneous catalysts based on a tran-
15 sition metal of groups 4 to 6 of the periodic table of
elements (in the form approved of by IUPAC and published
by "CRC Press Inc." in 1989, to which reference will be
made hereafter with the term "periodic table"), generally
known as Ziegler-Natta type catalysts. A more recent
20 group of catalysts active in the polymerization of α -
olefins consists of the combination of an oligomeric or-
gano-oxygenated derivative of aluminum (in particular
methylaluminoxane or MAO) with an η^5 -cyclopentadienyl com-
pound (metallocene) of a transition metal of the same
25 groups 4 to 6 of the periodic table, and especially group

groups 4 to 6 of the periodic table, and especially group 4. These latter catalysts are substantially soluble in hydrocarbon solvents and for this reason are often defined as "homogeneous", even if they are sometimes used in heterogeneous form by supporting them on an inert solid material. The characteristics of polymerization processes based on this type of catalytic systems can substantially differ from those of processes using heterogeneous catalysts of the Ziegler-Natta type, to such an extent that new olefinic polymers can be obtained, in certain cases, which could not be prepared with the traditional systems. Among the numerous publications available in literature on the matter, reference is made, for example, to the publications "Progress in Polymer Science", vol. 20 (1995), pages 309-367, and "Journal of Molecular Catalysis A: Chemical", vol. 128 (1998), pages 1-331, for a wide range of applications of the above techniques and results obtained.

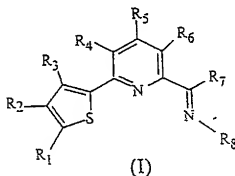
In the continuous attempt to improve the state of the art, new catalysis methods have been recently proposed for the oligo-/poly-merization of α -olefins based on complexes of "heavy" transition metals, i.e. of groups 8 to 10 of the periodic table.

Finally, studies are being increasingly more directed towards catalysts consisting of transition metals

complexed with nitrogenated chelating ligands useful for both the polymerization of ethylene and for its copolymerization with alpha-olefins and with polar comonomers. A recent review on the subject is provided in Chemical Reviews, 2000 (Steven D. Ittel, Lynda K. Johnson, Vol. 100, Nr. 4, pages 1169-1203).

A new group of ligands has now been found, together with the relative complexes with transition metals useful in the oligomerization and/or polymerization of ethylene and α -olefins.

In accordance with this, the present invention relates to ligands having general formula (I)



wherein R_1 , R_2 , R_3 , R_4 , R_5 and R_6 , the same or different, are selected from hydrogen, halogen, C_1 - C_{10} alkyl, C_6 - C_{15} aryl optionally halogenated, or adjacent pairs of R_i groups (with i ranging from 1 to 6) are bound to each other to give cyclic hydrocarbon structures condensed with the thiophene or pyridine ring;

25 R_7 is selected from H, C_1 - C_{10} alkyl, C_6 - C_{12} aryl;

R_8 is selected from C_1 - C_{10} alkyl and C_6 - C_{15} aryl.

In the preferred embodiment, R_3 , R_4 , R_5 , R_6 , R_7 are selected from H and C_1 - C_{10} alkyl radicals, R_8 is a C_6 - C_{15} aryl radical.

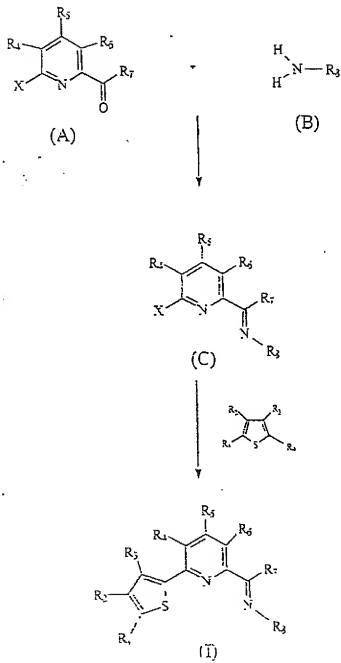
- 5 In the even more preferred embodiment, $R_3 = R_4 = R_5 = R_6 = H$, $R_7 = C_1$ - C_{10} alkyl; $R_8 =$ phenyl as such or alkyl substituted.

More specifically, an object of the present invention relates to:

- 10 ***) a ligand having general formula (I) wherein $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = H$; $R_7 = CH_3$; $R_8 = 2,6$ -diisopropylphenyl;
- ****) a ligand having general formula (I) wherein $R_1 = C_2H_5$; $R_2 = R_3 = R_4 = R_5 = R_6 = H$; $R_7 = CH_3$; $R_8 = 2,6$ -diisopropylphenyl;
- 15 ****) a ligand having general formula (I) wherein $R_1 = 9$ -anthryl; $R_2 = R_3 = R_4 = R_5 = R_6 = H$; $R_7 = CH_3$; $R_8 = 2,6$ -diisopropylphenyl;
- ****) a ligand having general formula (I) wherein $(R_1-R_2) = -(-CH=)_4-$; $R_3 = R_4 = R_5 = R_6 = H$; $R_7 = CH_3$; $R_8 = 2,6$ -
- 20 diisopropylphenyl;

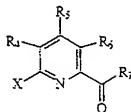
The compounds having general formula (I) can be obtained according to the process described in scheme (S).

SCHEME S



In accordance with this, the present invention relates to a process for the preparation of ligands having
 5 general formula (I) which comprises:

i) a first step which consists in the condensation of halogen acyl-pyridine having general formula (A),



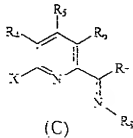
(A)

wherein X is a halogen, preferably bromine, R4, R5, R6 and R7 having the meaning defined above, with the primary
 15 amine, preferably aromatic, having general formula (B),



(B)

20 wherein R8 has the meaning indicated above, to give the halogen imino-pyridine having general formula (C);



(C)

ii) a second step which consists in the reaction of the halogen imino-pyridine having general formula (C) with the thiophene derivative having general formula (D),
5 wherein R_1 , R_2 , R_3 have the meaning defined above and R_4 is an organometallic radical bound to the thiophene ring



10 thus obtaining the compound having general formula (I) object of the present invention.

As far as the halogen acyl-pyridine having general formula (A) is concerned, this can be prepared according to techniques known to experts in the field. In particular, the synthesis of compounds (A) is described by
15 Parks, J.E. et al.; J. Organomet. Chem., 56, 53-66 (1973) and by Peterson M.A. et al.; J. Org. Chem., 62, 23, 8237-8239 (1997). The bromine acyl-pyridine (compound having general formula I wherein $X = \text{Br}$, $R_1 = R_2 = R_3 = \text{H}$; $R_4 =$
20 CH_3) can be typically prepared, see the experimental part, by the reaction of 2,6-dibromine pyridine with N,N-dimethyl acetamide in the presence of Lithium butyl.

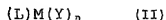
With respect to step (i) of the process of the present invention, this consists in the condensation, well
25 known to experts in the field, of an acetyl derivative

with a primary amine, preferably aromatic (R_9 = phenyl or mono or polyalkyl substituted phenyl). The condensation is typically effected in mass, i.e. without a solvent, preferably in the presence of an excess of amine, at temperatures higher than 100°C, thus favouring the removal of the water formed as by-product. At the end of step (i) the halogen imino-pyridine (C) is obtained.

Step (ii) of the process of the present invention consists in the reaction of the halogen imino-pyridine having general formula (C) with the thiophene derivative having general formula (D). In the preferred embodiment R_9 is an organometallic radical selected from alkyl derivatives of tin or other metals such as Li, Mg, Zn, Hg, preferably tin.

Step (ii) consists in the reaction of halogen imino-pyridine (C), preferably bromine imino-pyridine, with the thiophene derivative (D), directly or in the presence of catalysts, for example palladium tetrakis-triphenyl-phosphine. The reaction produces the ligand having general formula (I).

The present invention also relates to complexes having general formula (II)



wherein

L represents the ligand having general formula (I),

M is a metal selected from transition metals, i.e. metals of groups 3 to 12, preferably from 4 to 10, of the periodic table, and lanthanides; the above metal M being in oxidation state "s" positive different from zero, generally between 1 and 4;

Y is selected from groups of an anionic nature bound to the metal as anion in ionic couple or with a covalent bond of the "σ" type;

n expresses the number of Y groups sufficient for neutralizing the formal oxidation charge "s" of the metal M.

Typical but non-limiting examples of complexes having general formula (II) are indicated in the experimental part.

In the preferred embodiment of the present invention, M is selected from metals of groups 4 to 10 of the periodic table. Even more preferably, M is selected from metals of groups 8 and 9, particularly Cobalt, Iron, Ruthenium, Rhodium, Iridium in oxidation states from +2 to +3. Cobalt and Iron in oxidation state +2 are particularly suitable.

The symbol Y in formula (II) indicates groups (or ligands) of an ionic nature of the complex claimed. It is known that transition metals and lanthanides rarely form compounds and complexes of an exclusively ionic nature, the bond between metal and ligand being of an ionic-

covalent nature or totally covalent, in some cases. The symbol Y in formula (II) therefore relates to ligands of an anionic nature, which are normally bound to the metal M with a bond of a mainly covalent nature. The term $(Y)_n$ generally indicates the combination of ligands of an anionic nature, regardless of the actual number and type of Y present in the compound having formula (II). Y ligands different from each other are included in the above definition. Polyvalent or polydentate $(Y)_n$ ligands, for example oxalate, sulfate, phthalate groups, are also included in the scope of the present invention.

Examples of groups of $(Y)_n$ ligands of an anionic nature which can form compounds having formula (II) are halides, especially chloride and bromide, sulfates, and acid sulfates, alkyl- and aryl-sulfonic groups, phosphates and polyphosphates, alkyl- and aryl-phosphonic groups, hydride, linear, cyclic or branched alkyl groups having from 1 to 15 carbon atoms, such as methyl, ethyl, butyl, isopropyl, isoamyl, octyl, decyl, benzyl, cyclopentyl, cyclohexyl, 4-methylcyclohexyl, alkylsilyl groups having from 1 to 20 carbon atoms, such as, for example, trimethylsilyl, triethylsilyl or tributylsilyl, aryl groups having from 6 to 15 carbon atoms, such as phenyl or tolyl, alkoxyl or thioalkoxyl groups having from 1 to 10 carbon atoms, such as methoxyl, ethoxyl, iso- or sec-

butoxyl, ethylsulfide, carboxylate or dicarboxylate groups, such as acetate, trifluoroacetate, propionate, butyrate, pivalate, stearate, benzoate, oxalate, malonate, phthalate, or again, a dialkylamide group having
5 from 2 to 15 carbon atoms, such as diethylamide, dibutylamide, or alkylsilylamide, such as bis(trimethylsilyl)amide or ethyltrimethylsilylamide, divalent organic groups such as the trimethylene or tetramethylene group, or the ethylenedioxy group.

10 Groups or ligands different from each other can also be present, if desired, such as, for example, a chloride and a carboxylate or alkoxide group. The Y groups can be selected so as to make the complex having formula (II) sufficiently soluble in the solvents used during the
15 oligo- or polymerization process of ethylene, especially in the case of processes in solution.

In certain cases however the solubility of the complex is irrelevant, as in the case of supported complexes. In this latter case, the group of an anionic nature (Y) may also have an anionic function chemically
20 bound to the carrier. Examples of supported complexes and their preparation are provided in the experimental part.

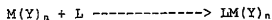
A further object of the present invention relates to a process for preparing complexes having general formula
25 (II) which comprises putting the ligand L having general

formula (I) in contact with a salt of the selected metal M, wherein M has the meaning defined above, preferably in the presence of an inert liquid.

For example, it is possible to start from the salt
5 of the metal M dissolved in an inert solvent (for example an alcohol or an ether). The stoichiometric quantity of the ligand L is added to this solution. The complex thus formed can be separated according to techniques known to experts in the field, for example crystallization or pre-
10 cipitation by means of a non-solvent, and subsequent separation by filtration or decanting. The above complex is usually formed rapidly and in more or less quantitative yields already under bland temperature conditions.

The complex having general formula (II) can also be
15 prepared in situ, without previous isolation.

The reaction is schematically as follows:



For simplicity of production and conservation of the respective complexes, the chlorine, bromine, alkoxide and
20 carboxylate groups (having from 2 to 15 carbon atoms) are preferred Y groups.

The following examples are provided for a better understanding of the present invention.

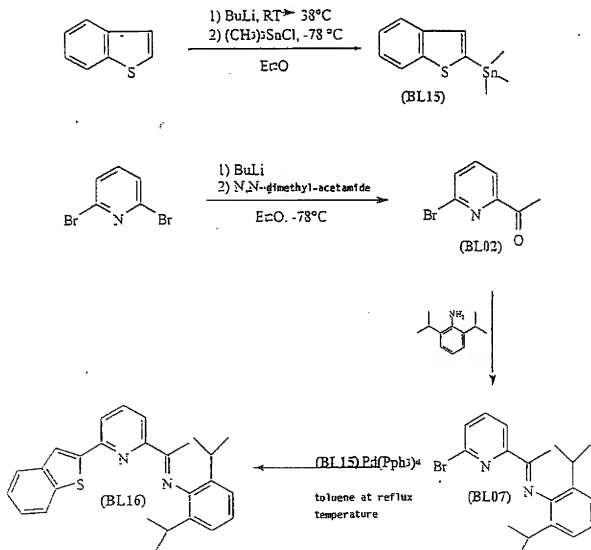
EXAMPLES

25 EXAMPLE 1 - Synthesis of the ligand having general for-

mula (I) called (BL16).

This synthesis is carried out starting from benzo-
thiophene according to scheme 1.

Scheme 1



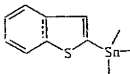
5

Synthesis of (BL15)

- 13.1 ml of BuLi 1.6 M in hexane (21.0 mmol), are added dropwise, at 0°C and in about 15', to a solution of 2.486 g (20.0 mmol) of benzothiophene in 50 ml of THF.
- 10 The whole mixture is left under stirring at room temperature for 10', and is then brought to reflux temperature. After 45' the mixture is cooled to -78°, 4.38 g (22.0 mmol) of solid (CH₃)₃SnCl are added and the mixture is left under stirring, at this temperature for 1 h.
- 15 The mixture is then rapidly brought to room temperature, diluted with 100 ml of CH₂Cl₂, washed with 2x50 ml of H₂O, 2x50 ml of a saturated solution of NaHCO₃, and again with 2x50 ml of H₂O.

- The organic phase is anhydriified with Na₂SO₄, and, on removing the solvent at reduced pressure, 5.10 g (17.0 mmol, yield 85%) of (BL15) are obtained as a limpid light orange-coloured oil.

(BL15)



25

$C_{11}H_{14}SSn$

FW 296.99 g mol⁻¹

¹H NMR (CDCl₃): δ = 0.55 (s, 9H, Sn(CH₃)₃); 7.34-7.47 (m, 2H, CH Ar); 7.53 (s, 1H, CH Ar); 7.90-8.02 (m, 2H, CH Ar)

5 ¹³C NMR (CDCl₃): δ = -7.54 (9C; Sn(CH₃)₃); 122.71 (1C, CH Ar); 123.60 (1C, CH Ar); 124.31 (1C, CH Ar); 124.63 (1C, CH Ar); 132.69 (1C, CH Ar); 141.12 (1C, C Ar); 141.78 (1C, C Ar); 144.98 (1C, C Ar).

Synthesis of BL02

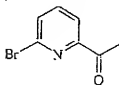
10 A solution of 7.107 g (30.00 mmol) of 2,6-dibromopyridine in 130 ml of dist. Et₂O is cooled, under a stream of N₂, to -78°C and 18.8 ml (30.0 mmol) of a solution 1.6 M of BuLi in hexane are added dropwise, in about 20'. After 30' 3.1 ml (33.0 mmol) of N,N-

15 dimethyl-acetamide are added and the mixture is left under stirring for 1 h and 15'. The mixture is slowly brought to room temperature, 40 ml of HCl 1N are added and the two phases are separated. The aqueous phase is extracted with Et₂O (3x30 ml) and the organic phases anhy-

20 drified with Na₂SO₄. The solution is then concentrated to a volume of about 10-12 ml and brought to 0°C.

After 12 h the crystals thus obtained are filtered and 4.061 g (21.60 mmol) of BL02 are obtained.

1-(6-Bromopyridin-2-yl)-ethanone*



Yield 72%

F.W. 200.03 g mol⁻¹

5 m.p. 44°C

IR: $\nu_{(C=O)}$ 1695 cm⁻¹

¹H NMR (CDCl₃): δ = 2.7 (s, 3H, Ar-C(O)CH₃); 7.6 (m, 2H, CH Ar.); 8.0 (dd, J = 6.5, 2.1 Hz, 1H, CH Ar.)

¹³C NMR (CDCl₃): δ = 26.4 (1C, Ar-C(O)CH₃); 121.1 (1C, CH Ar.); 132.4 (1C, CH Ar.); 139.8 (1C, CH Ar.); 142.0 (1C, CH Ar.); 154.9 (1C, CH Ar.); 198.5 (1C, Ar-C(O)CH₃).

* Ref: C. Bolm, M. Ewald, M. Felder, G. Schlingloff Chem. Ber. 1992, 125, 1169-1190.

Synthesis of BL07

15 0.60 g (3.0 mmoles) of BL02 and 1.77 g (pure tech. at 90%, 9.0 mmoles) of 2,6-diisopropylaniline are brought, without a solvent, to 105-110°C. After 16 h IR analysis reveals that the reaction has finished: a small amount of CH₂Cl₂ is added to the oily brown residue, which
20 is then crystallized from CH₃OH.

0.930 g (2.59 mmoles, yield 86%) of BL07 are obtained as yellow crystals.

N-[(E)-1-(6-bromo-2-pyridinyl)ethylidene]-2,6-

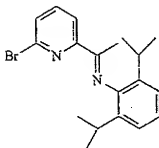
diisopropyl-aniline

or

N-[(E)-1-(6-bromo-2-

25 pyridinyl)ethylidene]-N-(2,6-diisopropylphenyl)amine

(BL07)



5

F.W. 359.32 g mol⁻¹

m.p. 126-128°C

IR: $\nu_{\text{C=H}}$, 1639 cm⁻¹

¹H NMR (CDCl₃): δ = 1.15 (d, J = 6.8 Hz, 6H, CH(CH₃)(CH₃)); 1.15 (d, J = 6.9 Hz, 6H, CH(CH₃)(CH₃)); 2.20 (s, 3H, C(N-Ar)CH₃); 2.64-2.77 (m, 2H, CH(CH₂)); 7.06-7.20 (m, 3H, CH Ar.); 7.59 (dd, J = 7.96, 1.3 Hz, 1H, CH Ar.); 7.65-7.72 (m, 1H, CH Ar.); 8.33 (dd, 1H, CH Ar., J = 7.5, 1.3 Hz)

¹³C NMR (CDCl₃): δ = 17.98 (1C, C(N-Ar)CH₃); 23.55 (2C, CH-CH₃); 23.90 (2C, CH-CH₃); 28.97 (2C, CH-(CH₃)₂); 120.73 (1C, CH Ar.); 123.72 (2C, CH Ar.); 124.50 (1C, CH Ar.); 129.89 (1C, CH Ar.); 136.34 (1C, C Ar.); 139.46 (1C, CH Ar.); 141.68 (1C, CH Ar.); 146.80 (1C, C Ar.); 158.09 (1C, CH Ar.); 166.62 (1C, C(N-Ar)CH₃).

Synthesis of the ligand BL16

0.055 g (0.047 mmoles) of Pd(PPh₃)₄ are added to a deaerated solution of 0.85 g (2.36 mmoles) of BL07 and 0.70 g (2.36 mmoles) of BL15 in 10 ml of toluene, and the mixture is brought to reflux temperature. After 2 h GC-MS

analysis shows the disappearance of the starting reagents. The solvent is evaporated at reduced pressure and a minimum quantity of CH_2Cl_2 is added to the solid yellow residue thus obtained, which is crystallized from

5 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$.

0.84 g (2.04 mmoles, yield 86%) of BL16 are obtained as yellow crystals.

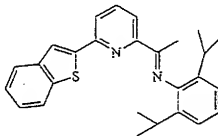
N-{(E)-1-[6-(1-benzothiophen-2-yl)-2-

pyridinyl]ethylidene}-2,6-diisopropylaniline or

10 N-{(E)-1-[6-(1-benzothiophen-2-yl)-2-

pyridinyl]ethylidene}-N-(2,6-diisopropylphenyl)amine

(BL16)



15

$\text{C}_{27}\text{H}_{29}\text{N}_2\text{S}$

F.W. 412.72 g mol^{-1}

m.p. 171-172°C

20 IR: $\nu(\text{C}=\text{N})$; 1643 cm^{-1}

^1H NMR (CDCl_3): δ = 1.19 (d, J = 6.7 Hz, 6H, $\text{CH}(\text{CH}_3)$ (CH_3)); 1.20 (d, J = 7.0 Hz, 6H, $\text{CH}(\text{CH}_3)$ (CH_3)); 2.35 (s, 3H, $\text{Ar}-\text{C}(\text{N}-\text{Ar})$ CH_3); 2.80 (m, 2H, $\text{CH}(\text{CH}_3)_2$); 7.10-7.25 (m, 3H, CH arom); 7.37-7.41 (m, 2H, CH arom); 7.83-7.93 (m,

25 5H, CH arom); 8.33 (dd, 1H, CH arom, J = 6.5, 2.4 Hz).

^{13}C NMR (CDCl_3): δ = 17.94 (1C, Ar-C(N-R) $\underline{\text{CH}}_3$); 23.71 (2C, CH($\underline{\text{CH}}_3$) ($\underline{\text{CH}}_3$); 24.02 (2C, CH($\underline{\text{CH}}_3$) ($\underline{\text{CH}}_3$); 29.07 (2C, $\underline{\text{CH}}$ -($\underline{\text{CH}}_3$) ($\underline{\text{CH}}_3$); 120.73 (1C, $\underline{\text{CH}}$ Ar.); 121.01 (1C, $\underline{\text{CH}}$ Ar.); 121.86 (1C, $\underline{\text{CH}}$ Ar.); 123.29 (1C, $\underline{\text{CH}}$ Ar.); 123.79 (2C, $\underline{\text{CH}}$ Ar.); 124.42 (1C, $\underline{\text{CH}}$ Ar.); 124.91 (1C, $\underline{\text{CH}}$ Ar.); 125.27 (1C, $\underline{\text{CH}}$ Ar.); 125.84 (1C, $\underline{\text{CH}}$ Ar.); 136.54 (2C, $\underline{\text{C}}$ Ar.); 137.85 (1C, $\underline{\text{CH}}$ Ar.); 141.30 (1C, $\underline{\text{C}}$ Ar.); 141.55 (1C, $\underline{\text{C}}$ Ar.); 145.81 (1C, $\underline{\text{C}}$ Ar.); 147.25 (1C, $\underline{\text{C}}$ Ar.); 152.09 (1C, $\underline{\text{C}}$ Ar.); 156.72 (1C, $\underline{\text{C}}$ Ar.); 167.64 (1C, Ar- $\underline{\text{C}}$ (N-R) $\underline{\text{CH}}_3$).

10 EXAMPLE 2 - Synthesis of the ligand having general formula (I) called (BL14).

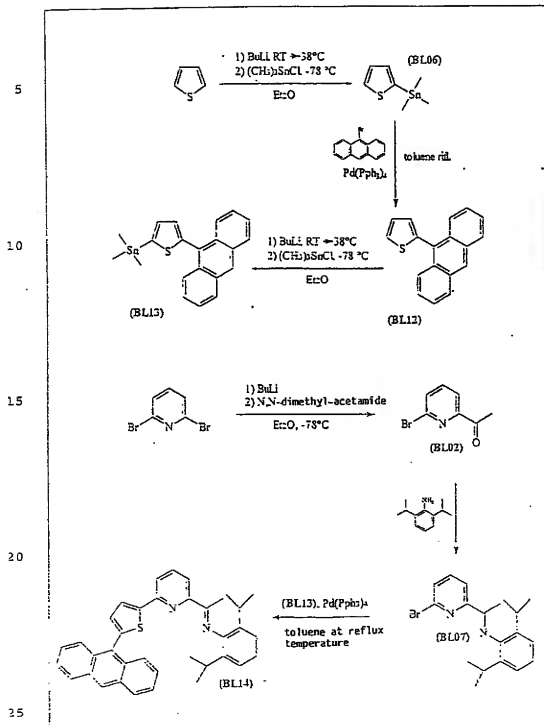
The reaction scheme (see scheme 2) is very similar to that of Example 1. The only difference is that the reaction starts from 2-(9-anthryl)thiophene (BL12) instead of benzothiophene.

15

20

25

Scheme 2



5

Synthesis of BL12

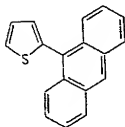
0.069 g (0.06 mmoles) of $\text{Pd}(\text{PPh}_3)_4$ are added to a
10 deaerated solution of 0.771 g (3.0 mmoles) of 9-bromo-
anthracene and 0.74 g (3.0 mmoles) of BL06 in 10 ml of
toluene, and the mixture is brought to reflux tempera-
ture. After 28 h GC-MS analysis shows the disappearance
of the starting reagents. The mixture is diluted with 30
15 ml of CH_2Cl_2 , washed with 2x30 ml of H_2O , 2x30 ml of a
saturated solution of NaHCO_3 and again with 2x30 ml of
 H_2O . The organic phase is anhydriified with Na_2SO_4 and upon
evaporation of the solvent at reduces pressure, a yellow-
orange solid residue is obtained, which is purified by
20 flash chromatography (SiO_2 , eluant petroleum ether, r_f =
0.25).

0.59 (2.27 mmoles), yield 76%) of BL12 are obtained
as a yellow solid.

2-(9-anthryl)thiophene

25

(BL12)

5 $C_{18}H_{12}S$ F.W. 260.36 g mol⁻¹

m.p. 111-113°C

¹H NMR (CDCl₃): δ = 7.21 (dd, J = 3.4, 1.2 Hz, 1H, CH Ar.); 7.33 (dd, J = 5.1, 3.4 Hz, 1H, CH Ar.); 7.38-7.54 (m, 4H, CH Ar.); 7.62 (dd, J = 5.1, 1.2 Hz, 1H, CH Ar.); 7.84-7.94 (m, 2H, CH Ar.); 8.01-8.13 (m, 2H, CH Ar.); 8.55 (s, 1H, CH Ar.)

¹³C NMR (CDCl₃): δ = 126.00 (2C, CH Ar.); 126.65 (2C, CH Ar.); 127.35 (2C, CH Ar.); 127.41 (1C, CH Ar.); 127.94 (1C, CH Ar.); 128.72 (1C, CH Ar.); 129.06 (2C, CH Ar.); 129.48 (1C, C Ar.); 130.13 (1C, CH Ar.); 131.97 (2C, C Ar.); 132.65 (2C, C Ar.); 139.71 (1C, C Ar.).

SYNTHESIS OF BL 13

Anhydrous glassware, all the operations are carried out under N₂.

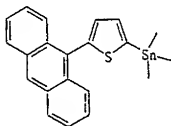
1.2 ml of BuLi 1.6 M in hexane (1.9 mmoles), are added dropwise, in about 15', to a solution of 0.40 g (1.53 mmoles) of BL12 in 50 ml of THF. The whole mixture is left under stirring at room temperature for 10', and is then brought to reflux temperature. After 45' the mix-

ture is cooled to -78° , 0.372 g (1.9 mmol) of solid $(\text{CH}_3)_3\text{SnCl}$ are added and the mixture is left under stirring, at this temperature for 1 h.

The mixture is then rapidly brought to room temperature, diluted with 100 ml of CH_2Cl_2 , washed with 2x50 ml of H_2O , 2x50 ml of a saturated solution of NaHCO_3 and again with 2x50 ml of H_2O .

The organic phase is anhydri-fied with Na_2SO_4 and, on removing the solvent at reduced pressure, 0.49 g (1.16 mmol, yield 76%) of (BL13) are obtained as an orange-coloured oil.

(BL13)



$\text{C}_{21}\text{H}_{20}\text{SSn}$

FW 423.15

^1H NMR (CDCl_3): δ = 0.48 (s, 9H, $\text{Sn}(\text{CH}_3)_3$); 7.31 (d, J = 3.2 Hz, 1H, CH Ar.); 7.38-7.52 (m, 5H, CH Ar.); 7.86-7.90 (m, 2H, CH Ar.); 8.02-8.07 (m, 2H, CH Ar.); 8.52 (s, 1H, CH Ar.)

^{13}C NMR (CDCl_3): δ = -7.36 (3C; $\text{Sn}(\text{CH}_3)_3$); 125.86 (2C, CH Ar.); 126.34 (2C, CH Ar.); 127.44 (2C, CH Ar.); 128.26 (1C, CH Ar.); 128.91 (2C, CH Ar.); 130.14 (1C, C Ar.);

131.34 (1C, C Ar.); 131.89 (2C, CH Ar.); 132.29 (2C, C Ar.); 135.78 (1C, C Ar.); 139.72 (1C, C Ar.); 145.31 (1C, C Ar.).

Synthesis of BL02

- 5 See the procedure described in Example 1.

Synthesis of BL07

See the procedure described in Example 1.

Synthesis of the ligand BL14

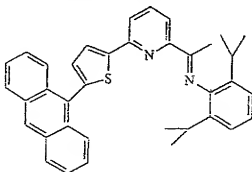
- 0.024 g (0.02 mmoles) of Pd(PPh₃)₄ are added to a
 10 deaerated solution of 0.45 g (1.06 mmoles) of BL07 and
 0.38 g (1.06 mmoles) of BL13 in 10 ml of toluene, and the
 mixture is brought to reflux temperature. After 18 h the
 solvent is evaporated at reduced pressure and a minimum
 quantity of CH₂Cl₂ is added to the oily residue thus ob-
 15 tained, which is crystallized from CH₂Cl₂/CH₃OH.

0.35 g (0.65 mmoles, yield 61%) of BL14 are obtained
 as yellow-beige crystals.

N-(2,6-diisopropylphenyl)-N-((E)-1-{6-[5-(9-anthryl)-2-
 thienyl]-2-pyridinyl}ethylidene)aniline or

- 20 N-(2,6-diisopropylphenyl)-N-((E)-1-{6-[5-(9-anthryl)-2-
 thienyl]-2-pyridinyl}ethylidene)-N-phenylamine

(BL14)





m.p. 243-244°C

5 IR: $\nu_{\text{C=N}}$ 1643 cm^{-1}

F.W. 538.88 g mol^{-1}

^1H NMR (CDCl_3): δ = 1.14 (d, J = 6.9 Hz, 6H, $\text{CH}(\text{CH}_3)$ (CH_3)); 1.17 (d, J = 6.8 Hz, 6H, $\text{CH}(\text{CH}_3)$ (CH_3)); 2.23 (s, 3H, $\text{Ar-C}(\text{N-R})\text{CH}_3$); 2.70-2.84 (m, 2H, $\text{CH}(\text{CH}_3)$); 7.05-7.20
 10 (m, 3H, CH Ar.); 7.23 (d, J = 3.6 Hz, 1H, CH Ar.); 7.41-7.53 (m, 4H, CH Ar.); 7.86-7.90 (m, 3H, CH Ar.); 8.29 (dd, J = 5.3, 3.3 Hz, 1H, CH Ar.); 8.56 (s, 1H, CH Ar.)

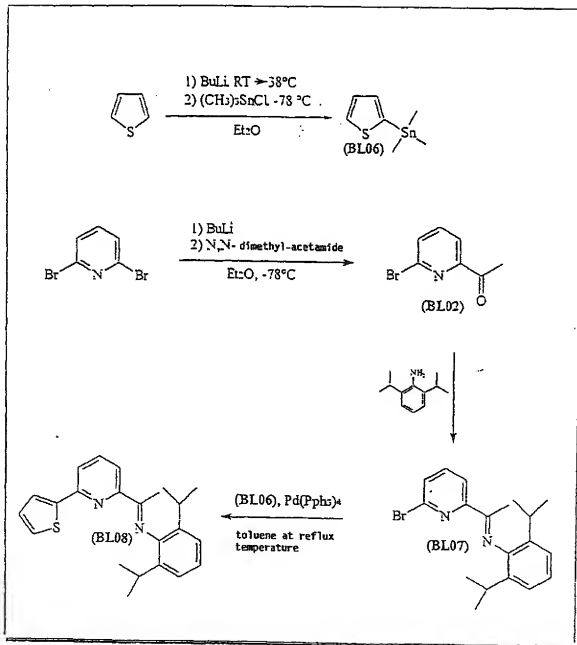
^{13}C NMR (CDCl_3): δ = 17.78 (1C, $\text{Ar-C}(\text{N-R})\text{CH}_3$); 23.58 (2C, $\text{CH}(\text{CH}_3)$ (CH_3); 23.90 (2C, $\text{CH}(\text{CH}_3)$ (CH_3); 28.93 (2C, $\text{CH}(\text{CH}_3)$ (CH_3);
 15 (CH₃); 119.93 (1C, CH Ar.); 120.02 (1C, CH Ar.); 123.64 (2C, CH Ar.); 124.21 (1C, CH Ar.); 125.32 (1C, CH Ar.); 125.98 (2C, CH Ar.); 126.69 (2C, CH Ar.); 127.19 (2C, CH Ar.); 128.81 (1C, CH Ar.); 129.03 (2C, CH Ar.); 131.27 (1C, CH Ar.); 131.88 (2C, C Ar.); 132.30 (2C, C Ar.);
 20 136.45 (2C, C Ar.); 137.96 (1C, CH Ar.); 142.25 (1C, C Ar.); 146.86 (1C, C Ar.); 147.17 (1C, C Ar.); 152.08 (1C, C Ar.); 156.65 (1C, C Ar.); 167.63 (1C, $\text{Ar-C}(\text{N-R})\text{CH}_3$).

EXAMPLE 3 - Synthesis of the ligand having general formula (I) called (BL08)

25 The reaction scheme (Scheme 3) is very similar to

that of Example 2. The only difference is in the use of thiophene instead of 2-(9-anthryl)thiophene.

Scheme 3



5

10

SYNTHESIS OF BL06

Anhydrous glassware, all the operations are carried out under N_2 .

7.5 ml (12.0 mmoles) of BuLi 1.6 M in hexane are
15 added dropwise, at room temperature, in about 15', to a
solution of 0.840 g (10.0 mmoles) of thiophene in 15 ml
of anhydrous Et_2O . The mixture is brought to reflux tem-
perature (the colour of the solution changes from yellow
to mud brown) and, after 30' is cooled to -78° and 2.39 g
20 (12.0 mmoles) of $(CH_3)_3SnCl$ are added. After 1.1 h the
bath at $-78^\circ C$ is removed and the mixture is left to
slowly rise to room temperature. The resulting suspen-
sion is washed with 30 ml of H_2O , 30 ml of a saturated so-
lution of $NaHCO_3$, again with 2x30 ml of H_2O and is anhy-
25 drified with Na_2SO_4 . Upon evaporation of the solvent at

reduced pressure, 2.33 g (9.44 mmoles, yield 94%) of BL06 are obtained as an orange oil which can be used without further purification.

5 (BL06)



^1H NMR (CDCl_3): δ = 0.53 (s, 9H, $\text{Sn}(\text{CH}_3)_3$); 7.28-7.38 (m, 2H, CH Ar.); 7.72 (dd, 1H, CH Ar., J_1 = 4.4 Hz, J_2 = 1.0 Hz)

10 ^{13}C NMR (CDCl_3): δ = -7.62 (9C; $\text{Sn}(\text{CH}_3)_3$); 128.68 (1C, CH Ar.); 131.49 (1C, CH Ar.); 135.72 (1C, CH Ar.); 137.84 (1C, C Ar.).

Synthesis of BL02

See the procedure described in Example 1.

15 Synthesis of BL07

See the procedure described in Example 1.

Synthesis of the ligand BL08

0.359 g (F.W. 359.44, 1.00 mmole) of BL07 and 0.247 g (F.W. 246.93, 1.00 mmole) of BL06 are dissolved in 5 ml of toluene and the resulting solution is deaerated in a stream of N_2 . 0.030 g (F.W. 1155.58, 0.026 mmole) of $\text{Pd}(\text{PPh}_3)_4$ are then added and the mixture is brought to reflux temperature. After 2 h it is brought to room temperature and the brown solid present in suspension is
25 filtered. Upon evaporation of the solvent, a yellow crys-

talline solid is obtained, which is washed with 2x30 ml of methanol.

0.23 g of BL08 are obtained (0.64 mmoles, yield 64%).

N-(2,6-diisopropylphenyl)-N-{(E)-1-[6-(2-thienyl)-2-

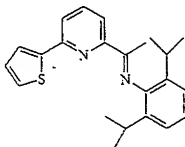
5 pyrid-ynyl]ethylidene} amine or

2,6-diisopropyl-N-{(E)-1-[6-(2-thienyl)-2-

pyridinyl]ethyl-idene} aniline.

(BL08)

10



$C_{23}H_{26}N_2S$

F.W. 362.66 g mol⁻¹

15 m.p. 140°C

IR: $\nu_{(C=N)}$ 1641 cm⁻¹

¹H NMR (CDCl₃): δ = 1.13 -1.20 (m, 12H, CH(CH₃)₂); 2.29 (s, 3H, Ar-CH₃); 2.66-2.98 (m, 2H, CH(CH₃)₂); 7.06-7.23 (m, 4H, CH arom); 7.42 (dd, J = 5.0, 1.1 Hz, 1H, CH arom); 20 7.67 (dd, J = 3.7, 1.1 Hz, 1H, CH arom); 7.75 (dd, J = 7.9, 1.5 Hz, 1H, CH Ar.); 7.79-7.87 (m, 1H, CH arom); 8.25 (dd, J = 7.4, 1.5 Hz, 1H, CH arom)

¹³C NMR (CDCl₃): δ = 17.85 (1C, Ar-C(N-R)CH₃); 23.64 (2C, CH(CH₃) (CH₃); 23.94 (2C, CH(CH₃) (CH₃); 28.99 (2C, CH(CH₃) (CH₃); 119.97 (1C, CH Ar.); 120.21 (1C, CH Ar.); 123.70 25 (CH₃);

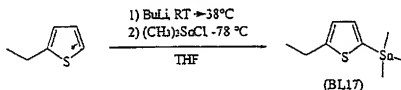
- (2C, CH Ar.); 124.26 (1C, CH Ar.); 125.32 (1C, CH Ar.);
 128.41 (1C, CH Ar.); 128.79 (1C, CH Ar.); 136.51 (2C, C
 Ar.); 137.86 (1C, CH Ar.); 145.73 (1C, C Ar.); 147.21
 (1C, C Ar.); 152.15 (1C, C Ar.); 156.57 (1C, C Ar.);
 5 167.70 (1C, Ar-C(N-R)CH₃).

EXAMPLE 4- Synthesis of the ligand (BL18)

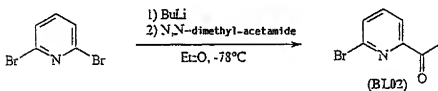
The reaction scheme (see scheme 4) is very similar to
 that of Example 3.

- The starting product is 2-ethyl thiophene instead of
 10 thiophene.

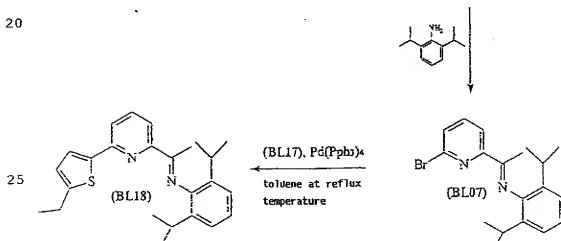
scheme 4



15



20



25

5

10

SYNTHESIS OF BL17

Anhydrous glassware, all the operations are carried out
15 under N_2 .

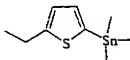
13.1 ml of BuLi 1.6 M in hexane (21.0 mmoles), are
added dropwise, in about 15', to a solution of 2.26 ml
(2.24 g, 20.0 mmoles) of 2-ethyl-thiophene in 60 ml of
THF. The whole mixture is left under stirring at room
20 temperature for 10', and is then brought to reflux tem-
perature. After 45' the mixture is cooled to -78° , 4.38 g
(22.0 mmoles) of solid $(CH_3)_2SnCl$ are added and the mix-
ture is left under stirring, at this temperature for 1 h.

The mixture is then rapidly brought to room tempera-
25 ture, diluted with 100 ml of CH_2Cl_2 , washed with 2x50 ml

of H₂O, 2x50 ml of a saturated solution of NaHCO₃ and again with 2x50 ml of H₂O.

The organic phase is anhydried with Na₂SO₄ and, on removing the solvent at reduced pressure, 5.28 g (19.2 mmoles, yield 96%) of (BL17) are obtained as a limpid orange oil.

(BL17)



10 C₉H₁₆SSn

FW 274.99 g mol⁻¹

¹H NMR (CDCl₃): δ = 0.40 (s, 9H, Sn(CH₃)₃); 1.38 (t, J = 7.4, 3H, CH₂-CH₃); 2.95 (qd, J = 7.4, 0.9 Hz, 2H, CH₂-CH₃); 6.97 (dt, J = 3.2, 0.9, 1H, CH Ar.); 7.08 (d, J = 3.2 Hz,

15 1H, CH Ar.)

¹³C NMR (CDCl₃): δ = -7.63 (3C; Sn(CH₃)₃); 16.82 (1C, CH₂-CH₃); 23.98 (1C, CH₂-CH₃); 125.50 (1C, CH Ar.); 135.31 (1C, C Ar.); 135.79 (1C, CH Ar.); 154.09 (1C, C Ar.)

Synthesis of BL02

20 See the procedure described in Example 1.

Synthesis of BL07

See the procedure described in Example 1.

Synthesis of BL18

0.552 g (2.0 mmoles) of BL17 and 0.72 g (2.0 mmoles) of BL07 are dissolved in 8 ml of toluene and the result-

ing solution is deaerated in a stream of N_2 . 0.046 g (0.0 mmoles) of $Pd(PPh_3)_4$ are then added and the mixture is brought to reflux temperature. After 4 h it is brought to room temperature and the brown solid present in suspension is filtered. Upon evaporation of the solvent, an oily residue is obtained to which 5 ml of CH_2Cl_2 are added and the mixture is crystallized from CH_3OH .

1st crop 0.38 g (0.98 mmoles, yield 49%)

2nd crop 0.26 g (0.67 mmoles, yield 33%)

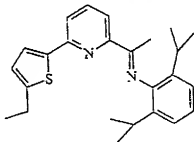
10 Total: 0.64 g, overall yield 82%, of (BL18)

N-{(E)-1-[6-(5-ethyl-2-thienyl)-2-pyridinyl]ethylidene}-2,6-diisopropylaniline or

N-(2,6-diisopropylphenyl)-N-{(E)-1-[6-(5-ethyl-2-thienyl)-2-pyridinyl]ethylidene} amine

15

(BL18)



20 $C_{25}H_{30}N_2S$

F.W. 390.73 g mol⁻¹

m.p. 121°C

IR: $\nu_{(C=N)}$ 1646 cm⁻¹

¹H NMR (CDCl₃): δ = 1.16 (d, J = 6.9, 12H, CH(CH₃)₂); 1.37

25 (t, J = 7.5, 3H, CH₂-CH₃); 2.29 (s, 3H, Ar-CH₃); 2.77

(sept, 2H, $\text{CH}(\text{CH}_3)_2$); 2.90 (q, $J = 7.5$, 2H, $\text{CH}_2\text{-CH}_3$); 6.83 (d, $J = 3.6$ Hz, 1H, CH Ar.); 7.06-7.21 (m, 3H, CH arom); 7.48 (d, $J = 3.6$, 1H, CH Ar.); 7.68 (dd, $J = 7.7$, 0.9 Hz, 1H, CH arom.); 7.75-7.82 (m, 1H, CH arom); 8.20 (dd, $J =$
 5 7.6, 0.9 Hz, 1H, CH arom).

^{13}C NMR (CDCl_3): $\delta = 16.61$ (1C, $\text{CH}_2\text{-CH}_3$); 17.85 (1C, Ar-C(N-R) CH_3); 23.61 (2C, CH(CH_3) (CH_3); 23.90 (2C, CH(CH_3) (CH_3); 24.49 (1C, $\text{CH}_2\text{-CH}_3$); 28.92 (2C, CH(CH_3) (CH_3); 119.42 (1C, CH Ar.); 119.71 (1C, CH Ar.); 123.64 (2C, CH Ar.); 124.17 (1C, CH Ar.); 125.22 (2C, CH Ar.); 136.51 (2C, C Ar.); 137.86 (1C, CH Ar.); 142.78 (1C, C Ar.); 147.24 (1C, C Ar.); 150.99 (1C, C Ar.); 152.42 (1C, C Ar.); 156.45 (1C, C Ar.); 167.74 (1C, Ar-C(N-R) CH_3).

EXAMPLE A - Synthesis of the complex BC03 starting from
 15 the ligand BLOS

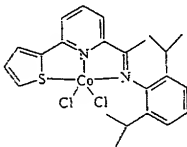
10 ml of distilled and deaerated n-butanol are brought to reflux temperature, 0.295 g (1.24 mmoles) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ are dissolved therein, under a stream of nitrogen, and the solvent is distilled to a total volume of
 20 the solution of about 7-8 ml. 0.450 g (1.24 mmoles) of (BLOS) are then added and the mixture is slowly brought to room temperature.

The green crystalline precipitate is filtered, washed with n-butanol, then with n-hexane previously
 25 deaerated and is finally transferred to a Schlenk tube.

0.58 g (1.18 mmoles; yield 95%) of BC03 are obtained as a green microcrystalline solid.

Reagents	F.W. (g mol ⁻¹)	molar ratio	mmoles	grams
BL08	362.66	1	1.24	0.450
CoCl ₂ ·6H ₂ O	237.93	1	1.24	0.295

BC03



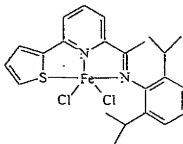
FW 492.50 g mol⁻¹

EXAMPLE B - Synthesis of the complex BC04 starting from the ligand BL08.

Products	F.W. (g mol ⁻¹)	molar ratio	mmoles	grams
BL08	362.66	1	1.24	0.450
FeCl ₂ ·4H ₂ O	198.82	1	1.24	0.247

0.50 g (1.02 mmoles; yield 82%) of BC04 are obtained as a red microcrystalline solid.

(BC04)



FW 489.41 g mol⁻¹

EXAMPLE C - Synthesis of the complex BC05 starting from
 5 the ligand BL18.

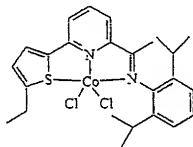
Products	F.W. (g mol ⁻¹)	molar ratio	mmoles	grams
BL18	390.73	1	0.51	0.200
CoCl ₂ ·6H ₂ O	237.93	1	0.51	0.116

10

0.207 g (0.40 mmoles; yield 78%) of BC05 are obtained as a green microcrystalline solid.

15

(BC05)

FW 520.57 g mol⁻¹

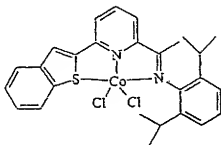
EXAMPLE D - Synthesis of the complex BC07 starting from
 20 the ligand BL16.

Products	F.W. (g mol ⁻¹)	molar ratio	mmoles	grams
BL16	412.72	1	0.485	0.200
CoCl ₂ ·6H ₂ O	237.93	1	0.462	0.110

25

0.20 g (0.37 mmoles; yield 80%) of BC07 are obtained as a green microcrystalline solid.

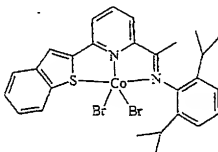
(BC07)



FW 520.57 g mol⁻¹

EXAMPLE E - Synthesis of the complex BC09

(BC09)



EXAMPLE alpha - Complex supported on polystyrene.

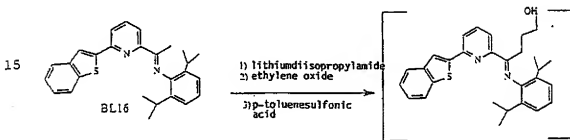
0.53 ml of a 1.5 M solution of LDA in THF are added, at 0°C, to a solution of 0.310 grams of ligand BL18 (FW 390.58 g mol⁻¹, 0.794 mmoles) in 20 ml of THF. After 3.5 hours at this temperature, 0.50 grams (0.8 mmoles Cl/g, 0.40 mmoles) of Merrifield chloromethylpolystyrene are added and the mixture is left under stirring at 0°C for 4

hours and at room temperature for 24 hours. The resin is then filtered, washed with 2x30 ml of THF, 3x30 ml of H₂O and 3x30 ml of CH₂Cl₂ and dried at reduced pressure. 0.35 grams of resin are obtained.

5 0.28 grams (0.80 mmoles) of CoCl₂·6H₂O are dissolved in 100 ml of n-butanol at 40°C and 0.35 grams of the functionalized resin obtained as described above are added. After 30 minutes the mixture is filtered, washed with 2x20 ml of n-butanol, 3x40 ml of petroleum ether and
10 the excess solvent is removed in a stream of N₂.

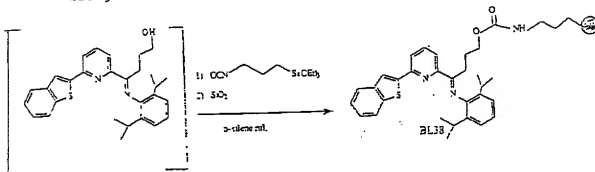
0.41 grams of green solid are obtained.

EXAMPLE beta - Complex supported on silica.



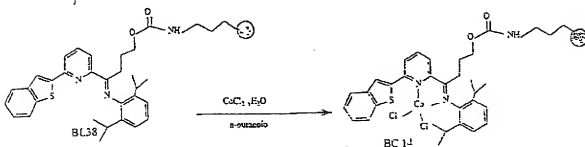
0.80 ml of a 1.5 M solution of lithiumdiisopropylamide in THF are added at 0°C to a solution of 0.5 g of the ligand BL16 (MW 412.72, 1.21 mmoles) in 20 ml of THF. After 3 hours at this temperature a solution of 0.06 g of ethylene oxide (MW 44.05, 1.36 mmoles) in 10 ml of THF are slowly added. The mixture is left under stirring
25 at 0°C for 5 hours. At the end, 0.258 g of p-

toluenesulfonic acid are added and then 0.29 g (1.2 mmoles) of di(3-isocyanatepropyl)-triethoxysilane dissolved in 30 ml of p-xylene and the resulting mixture is brought to reflux temperature.



After 12 hours 3.8 grams of silica are added and after a further 12 hours at reflux temperature the solid present in suspension is filtered, washed with 3x20 ml of p-xylene, 2x30 ml of n-hexane and the residual traces of solvent are eliminated at reduced pressure (40°C). 4.1 grams of BL38 are obtained.

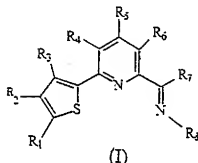
0.35 ml (1.47 mmoles) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ are dissolved in 100 ml of n-butanol at 40°C and 4.1 grams of the functionalized silica prepared above are added.



After 30 minutes the mixture is filtered, washed with 2x40
15 ml of n-butanol, 3x50 ml of petroleum ether and the excess
solvent is removed in a stream of N₂. 4.3 grams of BC14 are
obtained as a green solid.

CLAIMS

1. Ligands having general formula (I)



10 wherein R_1 , R_2 , R_3 , R_4 , R_5 and R_6 , the same or different, are selected from hydrogen, halogen, C_1 - C_{10} alkyl, C_6 - C_{15} aryl optionally halogenated, or adjacent pairs of R_i groups (with i ranging from 1 to 6) are bound to each other to give cyclic hydrocarbon structures condensed with the thio-
 15 phene or pyridine ring;

R_7 is selected from H, C_1 - C_{10} alkyl, C_6 - C_{15} aryl;

R_8 is selected from C_1 - C_{10} alkyl and C_6 - C_{15} aryl.

2. The ligands according to claim 1, wherein R_3 , R_4 , R_5 , R_6 , R_7 are selected from H and C_1 - C_{10} alkyl radicals, R_8 is a
 20 C_6 - C_{15} aryl radical.

3. The ligands according to claim 2, wherein $R_3 = R_4 = R_5 = R_6 = H$, $R_7 = C_1$ - C_{10} alkyl; $R_8 =$ phenyl as such or alkyl substituted.

4. A ligand according to claim 1, wherein $R_1 = R_2 = R_3 =$
 25 $R_4 = R_5 = R_6 = H$, $R_7 = CH_3$; $R_8 = 2,6$ -diisopropylphenyl.

5. A ligand according to claim 1, wherein $R_1 = C_2H_5$; $R_2 = R_3 = R_4 = R_5 = R_6 = H$, $R_7 = CH_3$; $R_8 = 2,6$ -diisopropylphenyl.

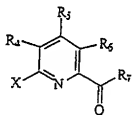
6. A ligand according to claim 1, wherein $R_1 = 9$ -anthryl; $R_2 = R_3 = R_4 = R_5 = R_6 = H$, $R_7 = CH_3$; $R_8 = 2,6$ -

diisopropylphenyl.

7. A ligand according to claim 1, wherein $(R_1-R_2) = -(CH_2)_4-$; $R_3 = R_4 = R_5 = R_6 = H$, $R_7 = CH_3$; $R_8 = 2,6$ -diisopropylphenyl.

8. A process for the preparation of the ligands having general formula (I) which comprises:

i) a first step which consists in the condensation of halogen acyl-pyridine having general formula (A),



(A)

wherein X is a halogen, R_4 , R_5 , R_6 and R_7 having the meaning defined above, with the primary amine having general for-

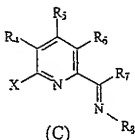
mula (B),



(B)

wherein R_6 has the meaning indicated above, to give the

halogen imino-pyridine having general formula (C);



- ii) a second step which consists in the reaction of the halogen imino-pyridine having general formula (C) with the thiophene derivative having general formula (D), wherein
- 10 R_1, R_2, R_3 have the meaning defined above and R_4 is an organometallic radical bound to the thiophene ring



- 15 thus obtaining the compound having general formula (I).
9. The process according to claim 8, wherein X is Br.
10. The process according to claim 8, wherein the primary amine is an aromatic amine.
11. The process according to claim 8, wherein R_4 is an organometallic radical selected from alkyl derivatives of tin, or other metals such as Li, Mg, Zn, Hg, preferably tin.
12. Complexes having general formula (II)



25 wherein:

- L represents the ligand having general formula (I),
M is a metal selected from transition metals, i.e. metals of groups 3 to 12 of the periodic table, and lanthanides; the above metal M being in oxidation state "s" positive
5 different from zero, generally between 1 and 4;
Y is selected from groups of an anionic nature bound to the metal as anion in ionic couple or with a covalent bond of the "σ" type;
n expresses the number of Y groups sufficient for neutral-
10 izing the formal oxidation charge "s" of the metal M.
13. The complexes according to claim 12, wherein M is a metal selected from metals of groups 4 to 10 of the periodic table.
14. The complexes according to claim 13, wherein M is a
15 metal selected from Cobalt and Iron in oxidation state +2.
15. The complexes according to claim 12, wherein Y is selected from chlorine, bromine, alkoxide and carboxylate (having from 2 to 15 carbon atoms).
16. A process for the preparation of the complexes having
20 general formula (II) which comprises putting the ligand L having general formula (I) in contact with a salt of the selected metal M, wherein M has the meaning defined above.
17. The process according to claim 16, characterized in that the reaction takes place in the presence of an inert
25 liquid.